# Synthesis and characterization of M-Zr bimetallic complex

**Xiang Ao supervised by Connie Lu**

## Introduction and Background

Bimetallic complexes with metal-metal bonds are being developed for small molecule activation processes. The strategy of pairing any two first-row transition metals is powerful as diverse properties such as redox potentials can be tuned systematically. The Lu research lab has developed and published several heterobimetallic complexes, which are shown in figure 1. The ligand with 3 fold symmetry was used as a scaffold to support two metals in these complex. In this project, one arm ligand designed by Lu Lab **HL** is synthesized and characterized, which has two active sites for forming a bimetallic complex. The reactions to synthesize Zr complex with **HL** were designed and performed. $^{1}$H NMR and $^{31}$P NMR were used to characterize the products. Chromium complex was successful synthesized by Lu Lab, the crystal structure is shown in figure below. The crystal structure of the Zr-Metal complex should be similar to the Zr –Co complex shown in figure 2, but with shorter Zr-Co bond length since an extra carbon is presented in ligand **HL**.

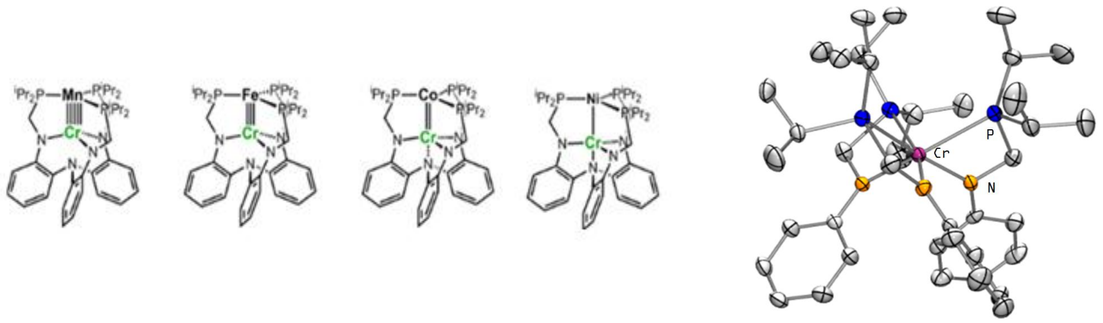
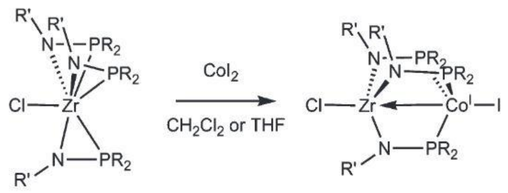



Figure 1.Heterobimetallic complexes M-Cr, where M= Mn, Fe, Co, and Ni, published in 2013（left),the solid state crystal structure of $CrL_3$, H atoms omitted for clarity, determined by X-Ray Crystallography(right).



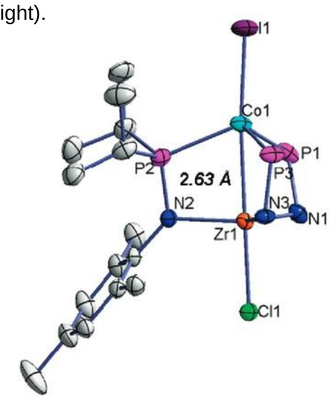
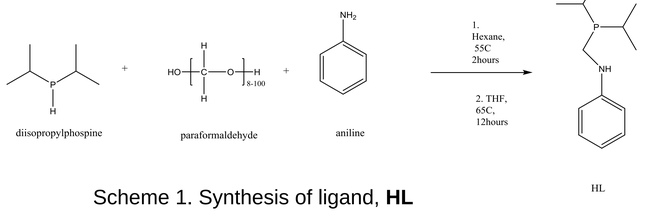




Figure 2. Zr-Cr complex synthesized by Thomas Lab, All hydrogen atoms and substituents on all but one ligand have been omitted for clarity.

## Experimental section

***Synthesis of HL, N-((diisopropylphosphanyl)methyl)aniline(4.1g, 89% yield).*:**




Scheme 1. Synthesis of ligand, **HL**

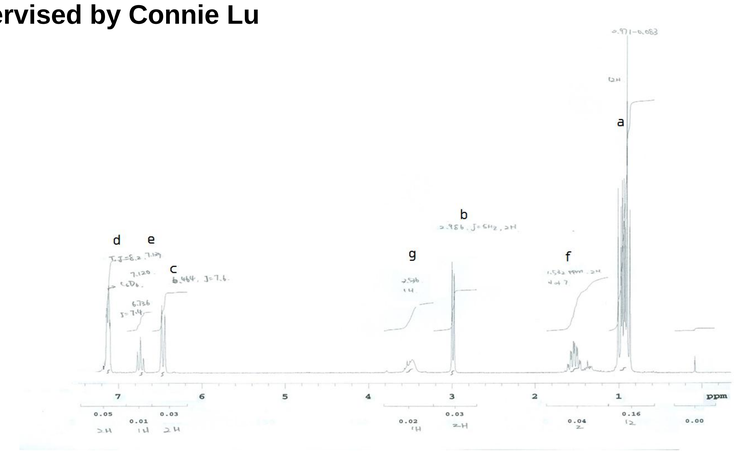
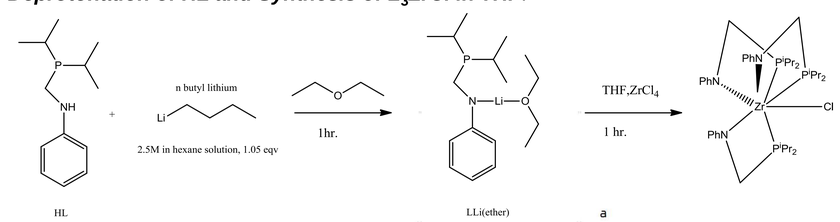
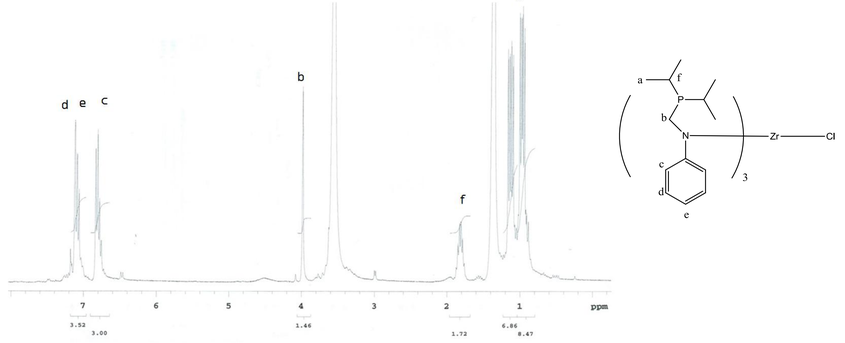



Figure 2. $^{1}$H NMR spectra of Ligand **HL**($C_6D_6$, 300MHz).

***Deprotonation of HL and Synthesis of $L_3ZrCl$ in THF***:




Scheme 2. Synthesis of ligand, HL, and $^{1}$H NMR spectra of Zr complex synthesized in THF ($C_6D_6$, 300MHz)

## Results and discussion

The spectra shows correct integration value corresponding to hydrogens in Zr complex proposed, and one large peak around -8 ppm shows one type of Phosphine is present. Crystallization of the complex was carried out with a few method such as ether vaporization, layering Zr complex in THF solution with pentane. However, no crystals formed. A few facts can be concluded for this reaction. The reaction cannot take place in ether, since $ZrCl_4$ doesn't dissolve in diethyl ether. Also cold temperatures are not suitable for this reaction, as the NMR spectrum showed only unreacted deprotonated ligand as the final product. Hot temperature conditions may help the reaction complete faster.

## Reference

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(2)Clouston, L. J.†; Siedschlag, R. B.†; Rudd, P. A.; Planas, N.; Hu, S.; Miller, A. D.; Gagliardi, L.; Lu, C. C.* J. Am. Chem. Soc. 2013, 135, 13142-13148.†co-first authors.
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## Acknowledgement

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